

Spin Glass Behavior in $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$

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The dynamics of the magnetic properties of polycrystalline $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru-1222) have been studied by ac susceptibility and dc magnetization measurements, including relaxation and ageing studies. Ru-1222 is a reported magneto-superconductor with Ru spins magnetic ordering at temperatures near 100 K and superconductivity in Cu-O₂ planes below $T_c \sim 40$ K. The exact nature of Ru spins magnetic ordering is still debated and no conclusion has been reached yet. In this work, a frequency-dependent cusp was observed in χ_{ac} vs. T measurements, which is interpreted as a spin glass transition. The change in the cusp position with frequency follows the Vogel-Fulcher law, which is commonly accepted to describe a spin glass with magnetically interacting clusters. Such interpretation is supported by thermoremanent magnetization (TRM) measurements at $T = 60$ K. TRM relaxations are well described by a stretched exponential relation, and present significant ageing effects.

The coexistence of superconductivity and magnetic order in ruthenium copper oxides $RuSr_2(Gd, Sm, Eu)_2Cu_2O_{10-\delta}$ (Ru-1222)^{1,2,3,4,5,6} and $RuSr_2(Gd, Sm, Eu)Cu_2O_{10-\delta}$ (Ru-1212) has attracted a lot of attention recently^{7,8,9,10,11,12,13,14,15,16,17,18,19}. But, besides this considerable interest, there are yet some unresolved questions about the exact type of magnetic order in these compounds. The difficulty about understanding the magnetic ordering in these systems is that different techniques like muon spin rotation (μ SR)⁹, magnetic resonance (MR)¹², neutron powder diffraction (NPD)^{13,16,17,18}, magnetization^{14,19} and nuclear magnetic resonance (NMR)¹⁵, though indicate towards canted antiferromagnetic ordering with a ferromagnetic component, they do not agree completely with each other. Although ferromagnetism and antiferromagnetism seems to be competing in these compounds^{13,16,17,18}, nobody speculates about the possibility of this competition to cause a frustration of the spin system, leading to a spin-glass scenario. The situation is especially unclear for the Ru-1222 family. For Ru-1222, though NPD results were reported recently²⁰, the magnetic structure has not been unveiled. Although the magnetic behavior of Ru-1222 has been considered to be analogous to the magnetic response for Ru-1212 samples, some recent results point towards various differences³.

In this work we explore the magnetic behavior of poly-

crystalline Ru-1222 samples by ac susceptibility ($\chi_{ac} = \chi' + i\chi''$), dc magnetization, and resistivity measurements. We observe a significant dependence of χ_{ac} on the frequency of the excitation field $h = h_0 \sin(\omega t)$, which is characteristic of spin glass systems. The temperature shift of the cusp in χ' follows the Vogel-Fulcher law, which describes the freezing temperature T_f of spin glasses with magnetically interacting clusters. Such interpretation is consistent with the observation of stretched exponential relaxations and the occurrence of ageing effects at temperatures below the magnetic ordering temperature.

I. EXPERIMENTAL DETAILS

The $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru-1222) sample was synthesized through a solid-state reaction route from RuO_2 , SrO_2 , Gd_2O_3 , CeO_2 , and CuO . Calcinations were carried out on the mixed powder at 1000, 1020, 1040, and 1060 °C each for 24 hours with intermediate grindings. The pressed bar-shaped pellets were annealed in a flow of high-pressure oxygen (100 atm) at 420 °C for 100 hours and subsequently cooled slowly to room temperature²¹. X-ray diffraction (XRD) patterns were obtained at room temperature (MAC Science: MXP 18 VAHF²²; CuK α radiation). Resistivity measurements

were made in the temperature range of 5 to 300 K using a four-point-probe technique. All ac susceptibility measurements were performed in a commercial PPMS (Physical Properties Measurement System), while for the dc measurements a SQUID magnetometer MPMS-5 were employed, both equipments made by Quantum Design company.

II. RESULTS AND DISCUSSION

Presently studied, Ru-1222 copper oxide sample crystallizes in a tetragonal structure of space group $I4/mmm$ with $a = b = 3.8327(7)$ Å and $c = 27.3926(8)$ Å. The X-ray diffraction pattern, Fig. 1, shows a single phase material, without any detectable impurity peak. The compound exhibited superconductivity ($R \approx 0$) below 40 K in electrical transport measurements²¹, as shown in the inset of Fig. 1. To recall the characteristic magnetic behavior of $Ru - 1222$, Fig. 2 displays the temperature dependence of both zero field cooled (ZFC) and field cooled (FC) dc magnetization measured at $H = 50$ Oe. The ZFC branch presents a pronounced peak at $T_p = 68$ K , just below the temperature where the ZFC and FC curves separated. The freezing temperature T_f , extracted from ac susceptibility measurements, is also indicated and will be discussed later. At $T_c = 45$ K is observed a kink in both ZFC/FC curves as the $Ru - 1222$ goes through its superconducting transition. The steady increase of the FC branch at low temperatures is interpreted as being caused by the paramagnetic response of the Gd ions. It is important to notice that some magnetic ordering starts to occur at a temperature $T^* = 160$ K much higher than T_p . This can be observed in the inset of Fig. 2, which shows an enlarged view of the magnetization curve at temperatures above T_p revealing a small hysteresis at these temperatures. Interestingly, both curves merge together again at a temperature around 80 K . The anomaly observed at T^* was previously reported as associated with an antiferromagnetic transition⁵, possibly in analogy to the magnetic ordering occurring in $Ru - 1212$. In the same temperature region we observed a small bump in $\rho \times T$ measurements (not shown). We speculate if this anomaly could indicate the appearance of spin clusters which at a lower temperature would have the magnetic moments frozen to originate a spin-glass system. In Fig. 3 we present a magnetization curve measured as a function of field, $M(H)$. The magnetization does not saturate even at the highest field 90 kOe, as shown in the inset of Fig. 3, which is consistent with what is expected for a spin-glass. The low field portion of the virgin branch of the hysteresis loop at 60 K displays an S shape, with a positive curvature at low fields, a typical characteristic of spin-glass systems. It is important to notice that $T = 60$ $K \gg T_c = 45$ K , thus this positive curvature at low field is not due to a superconductor contribution superimposed with a mag-

netic loop. Another striking characteristic of the virgin branch is that it stays outside the hysteresis loop. This unusual behavior was previously reported for cluster glasses with magnetic interacting clusters^{22,23,24}. It seems to be related with the more common displaced loop observed when the sample is field cooled^{22,23,25,26}, though a more recent work consider it should be due to a strong increase of the local surface anisotropy when the sample is cooled below a certain characteristic temperature, for a system of nanosized antiferromagnetic particles in an amorphous matrix²⁴.

The ac susceptibility (χ_{ac}) technique is a very powerful method to provide evidence of a spin-glass behavior. In this case, both components χ' and χ'' of χ_{ac} present a sharp, frequency dependent cusp. The position of the cusp in χ' defines the freezing temperature T_f , which is coincident with the temperature of the inflection point in χ'' . It is also well known that dc magnetic fields as low as a few hundreds of Oersted can round this cusp up. In Fig. 4 we present the ac susceptibility for our sample measured at $H_{dc} = 50$ Oe. The main frame of Fig. 4 presents the ZFC/FC temperature dependence of both χ' and χ'' for the frequency $\nu = 10000$ Hz. χ' presents a sharp drop at the superconducting transition temperature T_c and a sharp, frequency dependent peak at $T_f \approx 72$ K . The peak shifts to lower temperatures and its intensity increases as the frequency of the excitation field is decreased (see upper inset, Fig. 4). For the χ'' peak we observe the shift to lower temperatures as well as a decrease of its intensity with decreasing frequency (see lower inset of Fig. 4). The frequency dependence of both components is a typical feature of the dynamics of spin-glass systems. The coincidence of the temperature of both, the peak in χ' and the inflection point in the χ'' curve, is also verified in our data. The χ' component present a double anomaly in the 110 - 170 K range, but neither frequency nor thermal-magnetic history dependences are observed. The imaginary component does not present any significant feature in this temperature range. On the other hand, for temperatures below 60 K a clear separation of the ZFC/FC curves is observed in both components, although it is more prominent in χ'' .

To further verify the existence of a spin-glass behavior, we have studied the frequency dependence of χ_{ac} in more detail. A quantitative measure of the frequency shift is obtained from $\Delta T_f / [T_f \log(\omega)]$. This quantity varies in the range of 0.004 - 0.018 for spin-glass systems²⁷, while for superparamagnets²⁷ it is of the order of 0.3. From a set of FC susceptibility measurements at different frequencies, presented in the upper inset of Fig. 4, we could estimate $\Delta T_f / [T_f \log(\omega)] \approx 0.005$ for our Ru-1222 sample. Therefore, our data are consistent with the spin-glass hypothesis. There are basically two different possible interpretations of the spin-glass freezing: the first one assumes the existence of a true equilibrium phase transition at a finite temperature (canonical spin glasses)²⁸. The second interpretation assumes the existence of clusters and, in this case, the freezing

is a nonequilibrium phenomenon²⁹. For isolated clusters (superparamagnets), the frequency dependence of their freezing temperature (in this context more correctly referred as blocking temperature) has been predicted to follow an Arrhenius law

$$\omega = \omega_0 \exp[-E_a/k_B T_f], \quad (1)$$

where E_a is the potential barrier which separates two easy orientations of the cluster and ω is the driving frequency of the χ_{ac} measurement. However, for magnetically interacting clusters, a Vogel-Fulcher law has been proposed:

$$\omega = \omega_0 \exp[-E_a/k_B(T_f - T_0)], \quad (2)$$

where T_0 can be viewed as a phenomenological parameter which describes the intercluster interactions. Equation 2 implies a linear dependence of the freezing temperature with $1/\ln[(\omega\tau_0)^{-1}]$, $\tau_0 = 1/\nu_0 = 2\pi/\omega_0$. In Fig. 5 we present a Vogel-Fulcher plot, which shows that our data follows the expected linear behavior. From the best linear fit we obtained $\nu_0 \approx 1 \times 10^{12}$ Hz, $T_0 = 66.92$ K and $E_a = 76.92$ K.

Also, the existence of the spin-glass behavior has been checked through the time-dependent magnetic behavior of our sample. In this case, thermoremanent magnetization (TRM) measurements were performed. Since the behavior of a spin glass below T_f is irreversible and complicated by ageing processes, it is imperative to employ a well-defined H-T cycling procedure to obtain meaningful data. The precise procedure adopted in this work to measure the TRM relaxation was the following: the sample was field cooled ($H = 5000$ Oe) down from 200 K to 60 K; after temperature stabilization we waited for a certain time t_w . Thereafter the field was reduced to zero and the magnetization was recorded as a function of the elapsed time. The results for different values of t_w ($100 < t_w < 1000$ s) are presented in Fig. 6. Among the various functional forms that have been proposed to describe the magnetic relaxation in spin glasses, one of the most popular is the so-called *stretched exponential*

$$M(t) = M_0 - M_r \exp \left[- \left(\frac{t}{t_p} \right)^{1-n} \right], \quad (3)$$

where M_0 relates to an intrinsic ferromagnetic component and M_r to a glassy component mainly contributing to the relaxation effects observed. Both M_r and t_p (the time constant) depend upon T and t_w , while n is only a function of T . If $n = 0$ one has the Debye, single time-constant, exponential relaxation. On the other hand, for $n = 1$, one does not have any relaxation at all. The solid lines in Fig. 6 are the best fits of equation 3 to our experimental data, with parameters $4.38 \times 10^{-3} < M_0 < 4.49 \times 10^{-3}$ emu, $3.3 \times 10^{-4} < M_r < 3.7 \times 10^{-4}$ emu, and $n = 0.45$ (fixed for all fittings). The single parameter which presents a large variation with changes in the wait

time is the time constant t_p , which goes from $t_p = 1749$ s for $t_w = 100$ s to $t_p = 5214$ s for $t_w = 1000$ s. The changes observed in $M(t)$ measured for different values of t_w demonstrate the occurrence of ageing effects, what means that the physical system is in a metastable state. In the inset in Fig. 7 this point is emphasized by showing the relaxation rate $S(t) = \partial M / \partial \log(t)$. The shift in the minimum position of $S(t)$, expected to occur for a spin-glass system, is clearly observed.

III. CONCLUDING REMARKS

The frequency-dependent peak observed in the temperature dependence of the ac susceptibility χ_{ac} , combined with magnetic relaxation results, provides strong evidence of the important role of magnetic frustration in polycrystalline Ru-1222 to establish the existence of cluster glass properties over a significant temperature range. This is to be contrasted with the usual interpretation of the existence of long-range antiferromagnetic order with spin canting for both *Ru-1222* and *Ru-1212* samples. The microscopic reason why *Ru-1212* may present a long-range order while *Ru-1222* does not is not clear at this time. However, our results come in line with the recent findings of Živković *et al.*, Ref. 3, who have pointed out significant differences in the magnetic behavior of these two families of ruthenocuprates. Also, their results indicate the existence of a metastable magnetic state below the magnetic transition at T_f , which is in agreement with our interpretation of a cluster glass freezing at T_f .

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FIG. 1. Powder x-ray diffraction pattern for Ru - 1222 sample. Inset: $R(T)$ measurement at $H = 0$ showing the superconducting transition.

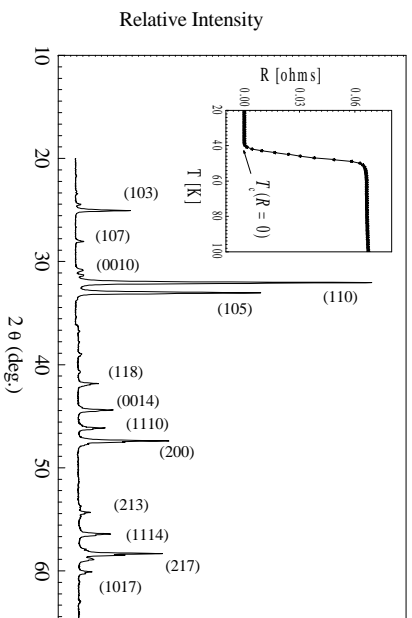
FIG. 2. Field cooled and zero field cooled temperature dependence of magnetization for $H = 50$ Oe. Inset: amplification of the $M(T)$ curves showing the small hysteresis at high temperatures.

FIG. 3. Low field portion of the $M(H)$ curve at $T = 60$ K. Inset: entire $M(H)$ curve for fields up to 90 kOe.

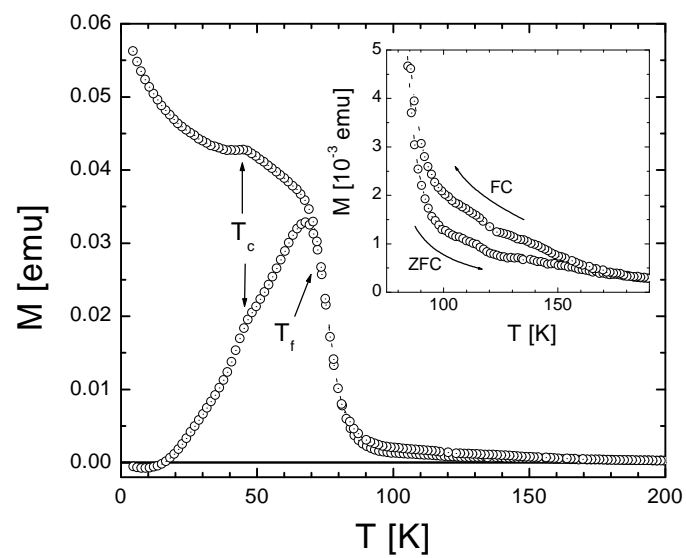
FIG. 4. Complex susceptibility as a function of temperature for $\nu = 10$ kHz (main panel). Upper (lower) inset shows the frequency dependence of the peak in the real (imaginary) component at the freezing temperature T_f .

FIG. 5. Variation of the freezing temperature T_f with the frequency of the ac field in a Vogel-Fulcher plot. The solid line is the best fit of Eq. 2.

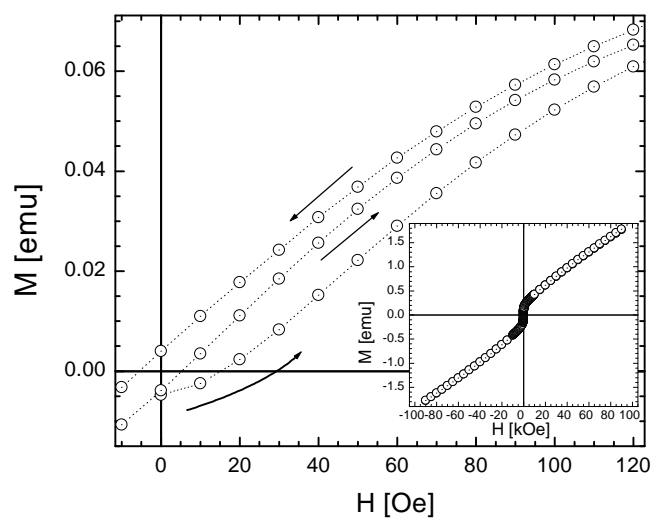
FIG. 6. Thermoremanent magnetization relaxation for $T = 60$ K and $t_w = 100$ s (squares), 500 s (circles), and 1000 s (triangles). The solid lines are the best fits of Eq. 3. Inset: relaxation rate $S(t) = \partial M / \partial \ln(t)$ for the relaxations presented in the main panel.



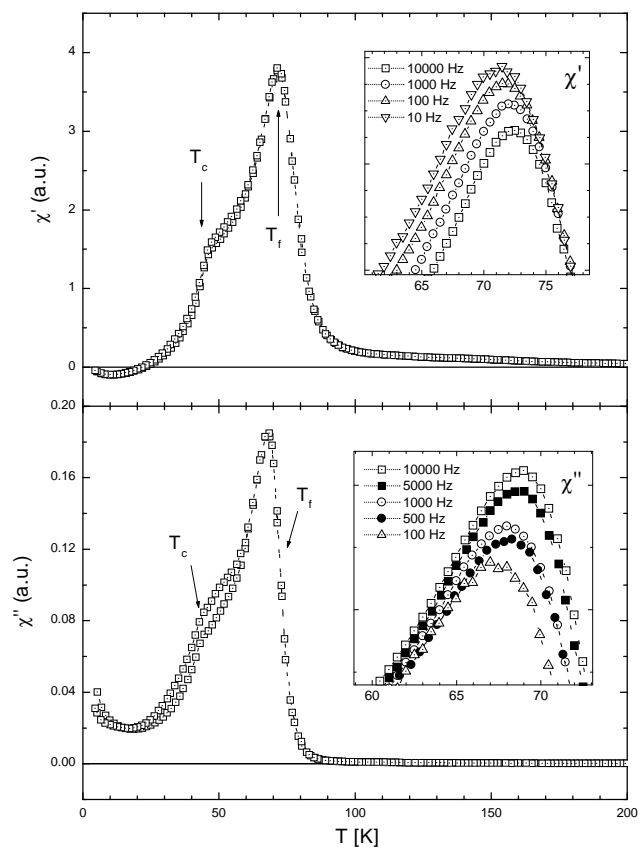
Cardoso et al. - Fig. 1



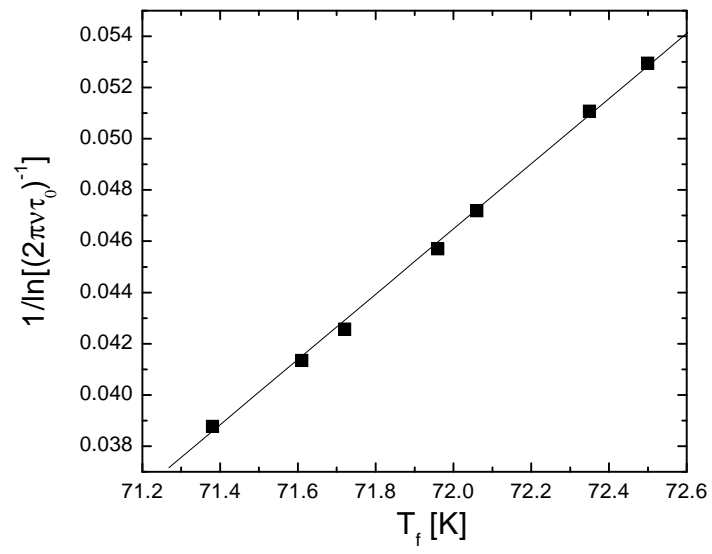
Cardoso et al. - Fig. 2



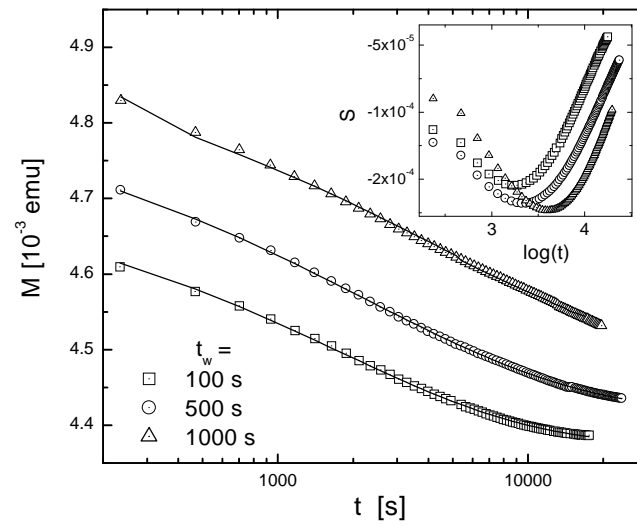
Cardoso et al. - Fig. 3



Cardoso et al. - Fig. 4



Cardoso et al. - Fig. 5



Cardoso et al. - Fig. 6